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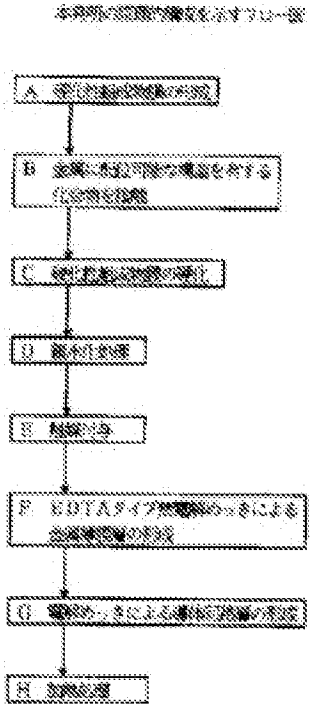
(54) METHOD OF FORMING MULTILAYERED CIRCUIT STRUCTURE AND SUBSTRATE HAVING MULTILAYERED CIRCUIT STRUCTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a method of forming multilayered circuit structure by which the adhesive property of a conductor circuit layer can be improved while the surface of an electrical insulating layer is kept in a flat state, and to provide a substrate having a multilayered circuit structure.

SOLUTION: After a film of a curable composition composed of an insulating polymer and a curing agent is formed as the outermost layer of an internal substrate, the electrical insulating layer is formed on the surface of the film of the curable composition by bringing a compound having coordination geometry to a metal into contact with the surface of the insulating layer and curing the film of the curable composition. Then the surface of



the formed electrical insulating layer is treated to have a hydrophilic property and a metallic thin film layer is formed on the surface of the insulating layer by using an ethylenediaminetetraacetic acid-copper complex. After the metallic thin film layer is formed, the conductor circuit layer containing the thin film layer is formed.

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]This invention relates to the base substance which has a formation method of multilayered circuit structure, and multilayered circuit structure, and in more detail, It is related with the base substance which has the formation method of multilayered circuit structure and multilayered circuit structure which have the feature in down stream processing for excelling in circuit pattern adhesion and forming a conductor circuit layer on a smooth electrical insulation layer.
[0002]
[Description of the Prior Art]A densification is increasingly requested more also from the circuit board used for the electronic device with the miniaturization of an electronic device, and multi-functionalization. In order to respond to the request of the densification of such a circuit board, it is common to multilayer a circuit board.
[0003]A multilayered circuit board usually laminates an electrical insulation layer on the surface of an inner layer board on which the conductor circuit layer was formed in the outermost layer, is obtained by forming a new conductor circuit layer on the electrical insulation layer concerned, and can also laminate an electrical insulation layer and several steps of conductor circuits if needed further.
[0004]In such a multilayered circuit board, in order to secure the life of a multilayered circuit board, it is important, the adhesion, i.e., pattern adhesion, of an electrical insulation layer and the conductor circuit pattern formed on it.
[0005]Then, various kinds of methods of roughening an electrical insulation layer as a method of acquiring such pattern adhesion (if necessary) Since JP,H11-23649,A, JP,H11-286562,A, and referring to the patent No. 2877110 gazette are adopted widely, the example is explained with reference to drawing 5 and drawing 6 here.

[0006]After laminating the epoxy resin layer 32 on refer to drawing 5 (a) 31, for example, the double-sided copper clad laminate which established the copper circuit (a graphic display is omitted) in the surface, the via hole (a graphic display is omitted) for connecting with the copper circuit which irradiated with ultraviolet laser radiation and was established in the double-sided copper clad laminate 31 is formed.

[0007]Drawing 5 (b) Subsequently it is immersed 3 ** into the solution which used NaOH and a surface-active agent as the main ingredients, and swelling processing of the epoxy resin layer 32 is carried out. A swelling layer is formed in the surface of the epoxy resin layer 32 of this swelling processing.

[0008]Drawing 5 (c) by subsequently immersing the double-sided copper clad laminate 31 3 ** into the desmear treatment solution which is an oxidizing solution which consists of a mixed solution of $KMnO_4$ and NaOH, Detailed unevenness is formed in the surface of the epoxy resin layer 32 while removing the residue generated in laser beam machining inside a via hole.

[0009]Subsequently, in the neutralized solution which contains hydrazine after carrying out rinsing treatment of the double-sided copper clad laminate 31, the double-sided copper clad laminate 31 is immersed, neutralization processing is carried out, and it ranks second, and again, after carrying out rinsing treatment of the double-sided copper clad laminate 31, the double-sided copper clad laminate 31 is immersed into a degreasing solution, and degreasing treatment is performed.

[0010]Drawing 5 (d) 3 **, subsequently, after carrying out rinsing treatment of the double-sided copper clad laminate 31, it is immersed into PURIDIPPU liquid, improve familiarity by the catalyst liquid in the catalyst process of a next step, and it ranks second, After carrying out rinsing treatment of the double-sided copper clad laminate 31, it is immersed into catalyst liquid and colloid substance $[(Pd)_m(Sn)_n(Cl)_l^-]$ of Sn and Pd 35 is deposited in the exposed surface of a copper circuit, the epoxy resin layer 32, and the swelling layer 33.

[0011]Drawing 6 (e) Subsequently, after carrying out rinsing treatment of the double-sided copper-clad lamination 31 board, it is immersed into accelerator liquid, Sn in a colloid substance is made to break away, and only Pd catalyst 36 is made to adhere to the exposed surface of a copper circuit, the epoxy resin layer 32, and the swelling layer 33 3 **.

[0012]Drawing 6 (f) by subsequently, performing non-electrolytic copper plating processing using the non-electrolytic copper plating liquid of a copper sulfate system which uses copper sulfate as the main ingredients 3 **, after carrying out rinsing treatment of the double-sided copper clad laminate 31, The plating seed layer which consists of the non-electrolytic copper plating layer 37 is formed in the exposed surface of a copper circuit, the epoxy resin layer 32, and the swelling layer 33.

[0013]drawing 6 (g) -- the electrolytic copper plating layer 38 is formed on the plating seed

layer exposed by subsequently performing electrolytic copper plating processing to the double-sided copper clad laminate 31 in which the non-electrolytic copper plating layer 37 was formed, 3 ** -- both via holes being embedded, and, [rank second and] A copper wiring is formed by etching the electrolytic copper plating layer 38 and the non-electrolytic copper plating layer 37 into a prescribed pattern. A multilayered circuit board is completed by the number of times which needs this process repeating.

[0014]Applying the adhesives for nonelectrolytic plating containing polymeric components, such as rubber and resin, on the electrical insulation layer after roughening as other means to improve adhesion is also examined (if necessary). Refer to JP,2001-192844,A, JP,2001-123137,A, and JP,H11-4069,A etc.

[0015]By these people's using polyimide as a resin layer, and adsorbing and returning metal ion at the ring breakage residue of polyimide, adhesion strength 0.6 kgf/cm needed practically is attained (being required -- if -- the 2nd time of Kumamoto area concentration type joint research "ultraprecise semiconductor Measurement Division technical development" technical symposium, and 2001 references).

[0016]However, by processing after such an electrical insulation layer was formed, when there was change of temperature or humidity, sufficient pattern adhesion was not necessarily acquired, but when shortening the life of a circuit board and the surface roughness of the roughened surface became small, adhesion might be low, and reliability might fall.

[0017]When a conductor circuit is formed for the conductor layer formed on the roughened above electrical insulation layers with an etching reagent, Since the ease of entering of an etching reagent changes with extensive ** of the interval of a conductor circuit and there is a problem that the process tolerance of a conductor circuit worsens, this situation is explained with reference to drawing 7.

[0018]After forming the non-electrolytic copper plating layer 42 by a nonelectrolytic plating method on the resin layer 41 which carried out the drawing 7 (a) reference roughening treatment, the electrolytic copper plating layer 44 is formed by the electrolysis plating method using the plating resist pattern 43.

[0019]Drawing 7 (b) 3 **, subsequently, after removing the plating resist pattern 43, the non-electrolytic copper plating layer 42 to expose is removed, and while forming the wiring 45-47 which consists of electrolytic copper plating layer 44 / the non-electrolytic copper plating layer 42, each wiring 45-47 is separated electrically.

[0020] Since the flow of an etching reagent is not smooth in refer to drawing 7 (c), however the place where the mutual interval of the wiring 45 and 46 is narrow and an etching rate falls, In order to remove thoroughly the non-electrolytic copper plating layer 42 to expose and to separate each wiring 45 and 46 electrically, it is necessary to lengthen etching time. Since the surface of the resin layer 41 is roughened especially, etching time becomes long, in order that

the thickness of the non-electrolytic copper plating layer 42 may be set to 3-8 micrometers in the portion which embedded the crevice and may remove this 3-8-micrometer non-electrolytic copper plating layer 42.

[0021]When it does so, in the place where the mutual interval of the wiring 46 and 47 is large, since the flow of an etching reagent becomes smooth, an etching rate becomes high, superfluous etching of the wiring 47 will be carried out, pattern shape will deteriorate, and process tolerance will fall.

[0022]Since the formed conductor circuit layer becomes non-flatness when the surface of an electrical insulation layer is roughened, in order to carry out an adhesion improvement, the electric-signal-transmission characteristic of a conductor circuit has the problem of getting worse under the influence of a skin effect in the high frequency region more than GHz. Incidentally, in the case of 1 GHz, in order to concentrate on a thickness of about 2 micrometers from the surface of a conductor layer, when surface unevenness is large, effectual transmission-line length becomes long and the electric-signal-transmission characteristic will get worse.

[0023]

[Problem to be solved by the invention]In order to solve such a problem, one of this invention persons, When forming wiring, without roughening the surface of a resin layer, it has found out that adhesion is securable by forming the layer containing the compound which can be configurated to metal on the surface of a resin layer in order to solve the problem of a fall of adhesion (if necessary, refer to Patent Application No. 2001-268847).

[0024]Then, this invention persons performed this time examination for raising the peel strength which is one of the indices of adhesion paying attention to the plating conditions in this method.

[0025]

[Means for solving problem]Drawing 1 is a flow chart showing the theoretic composition of this invention, and explains The means for solving a technical problem in this invention with reference to drawing 1 here. In the formation method of multilayered circuit structure, drawing 1 reference (1) this invention to the outermost layer of an inner layer board. After forming the hardenability constituent film which consists of an insulating polymer and a hardening agent (process A), contact the compound which has the structure which can be configurated to metal to said hardenability constituent membrane surface (process B), and it ranks second to it, After stiffening the hardenability constituent film concerned and forming an electrical insulation layer (process C), perform hydrophilization treatment on the surface of the obtained electrical insulation layer (process D), and it ranks second to it, After using an ethylenediaminetetraacetic acid-copper complex for the surface of said electrical insulation layer and forming a metallic thin film layer in it (process F), it is characterized by each (process

G) thing which forms the conductor circuit layer containing said metallic thin film layer and to do for a process owner.

[0026]Thus, a result of having inquired wholeheartedly so that this invention persons may get a multilayered circuit board which holds high pattern adhesion by a smooth electrical insulation layer top, When forming an electrical insulation layer, by forming a metal thin film using a specific complex, growing up plating and forming a conductor circuit layer on it, it finds out that the above-mentioned purpose is attained and came to complete this invention. Although a printed circuit board is typical as an inner layer board in this case, semiconductor substrates, such as a Si wafer, may be sufficient.

[0027]Although a catalyst grant process (the process E) follows in advance of the process F, in this catalyst grant process, it is desirable to use a catalyst of alkali complex structure.

[0028](2) In the above (1), this invention hydrophilization treatment (the process D), It is characterized by being the process of contacting a mixed solution and an electrical insulation layer which consist of not less than 65g/l. 150g/l. or less of potassium permanganate, and 0.75-N or more hydroxylation alkali of 1.5 N or less, and carrying out the surface treatment of the electrical insulation layer.

[0029]Thus, as for hydrophilization treatment which removes a weak boundary layer, it is desirable to carry out using a high concentration solution of an above-mentioned presentation, and its short time processing is especially desirable.

[0030](3) The hardenability constituent film as for which this invention consists of an insulating polymer formed in the outermost layer of an inner layer board, and a hardening agent in the above (1) or (2), or [piling up either / which consists of an insulating polymer and a hardening agent / the film state of a hardenability constituent, or a sheet-shaped Plastic solid on an inner layer board, and forming it] -- or, It formed by one method of whether apply and dry on the inner layer board surface, and the varnish which obtained the hardenability constituent which consists of an insulating polymer and a hardening agent by dissolving in a solvent is formed in it.

[0031](4) In the above (1) thru/or either of (3), this invention has a process (process H) to heat, after forming a conductor circuit layer (process G).

[0032]Thus, after forming a conductor circuit layer, adhesion strength can be increased by heating. This is considered because remaining stress is opened wide while a chemical bond promotes.

[0033](5) In the base substance which has multilayered circuit structure, this invention has the multilayered circuit structure manufactured by the formation method of the above (1) thru/or one multilayered circuit structure of (4). In this case, if an inner layer board is a printed-circuit board, a "base substance" will serve as a multilayered circuit board, and if an inner layer board is a semiconductor substrate, a "base substance" will serve as a semiconductor integrated

circuit device.

[0034]

[Mode for carrying out the invention]Here, with reference to drawing 2 and drawing 3, the suitable procedure of an embodiment of the invention is explained.

refer to drawing 2 (a) (process A) -- in order to form an electric insulating layer on the inner layer boards 11, such as a printed-circuit board which is a substrate with which the conductor circuit which consists of conductive metals was first formed in the surface, the hardenability constituent film 12 is formed. the thickness of the printed-circuit board used as the inner layer board 11 in this case -- for example -- 50 micrometers - 2 mm, preferably, it is 100 micrometers - 1 mm more preferably, and may be 1 mm 60 micrometers - 1.6 mm here.

[0035]The hardenability constituent film 12 in this case is a film of the hardenability constituent which consists of an insulating polymer which has electric insulation, and a hardening agent. As an insulating polymer, an epoxy resin, maleimide resin, an acrylic resin (meta), Diallyl phthalate resin, triazine resin, an alicyclic olefin polymer, an aromatic polyether polymer, a benz-cyclo-butene polymer, a cyanate ester polymer, a liquid crystal polymer, polyimide, etc. are mentioned. Also in these, an alicyclic olefin polymer, an aromatic polyether polymer, A benz-cyclo-butene polymer, a cyanate ester polymer, or polyimide is preferred, and an alicyclic olefin polymer or especially an aromatic polyether polymer is preferred, and an alicyclic olefin polymer divides and it is still more desirable.

[0036]As such an alicyclic olefin polymer, the ring-opening-polymerization object and its hydrogenation things of a norbornene system monomer, such as 8-ethyl-tetracyclo [4.4.0.$1^{2,5}$.$1^{7,10}$] dodec-3-ene, The addition polymer of a norbornene system monomer, the addition polymer of a norbornene system monomer and a vinyl compound, a monocycle cycloalkene polymer, an alicyclic conjugated diene polymer, a vinyl system alicyclic hydrocarbon polymer and its hydrogenation thing, the aromatic ring hydrogenation thing of an aromatic olefin polymer, etc. are mentioned. Also in these, the ring-opening-polymerization object and its hydrogenation thing of a norbornene system monomer, The aromatic ring hydrogenation thing of the addition polymer of a norbornene system monomer, the addition polymer of a norbornene system monomer and a vinyl compound, and an aromatic olefin polymer is preferred, and the hydrogenation thing of the ring-opening-polymerization object of a norbornene system monomer is preferred especially.

[0037]As for these polymers, it is preferred that it is what has the carboxyl group or carboxylic anhydride residue which carried out graft denaturation of carboxylic acid or the carboxylic anhydride compound, and was combined.

[0038]The hardening agent etc. which combine an ionicity hardening agent, a radical character hardening agent or ionicity, and radical character as a hardening agent, A general thing can be used and polyvalent epoxy compounds, such as a glycidyl ether type epoxy compound

especially like bisphenol A bis(propylene glycol glycidyl ether)ether, an alicyclic epoxy compound, and a glycidyl ester type epoxy compound, are preferred.

[0039]In order to promote a hardening reaction, it is preferred to use hardening accelerators and hardening auxiliary agents, such as a tertiary amine system compound and a 3 fluoridation boron complex compound, for the **** case for polyvalent epoxy compounds, for example as a hardening agent.

[0040]To the hardenability constituent concerning this invention, according to a request, fire retardant, an elasticity polymer, Heat-resistant stabilizer, weathering stabilizer, an antiaging agent, a leveling agent, a spray for preventing static electricity, a slipping agent, anti blocking agents, an antifogger, lubricant, a color, paints, natural oil, synthetic oil, a wax, an emulsion, a bulking agent, an ultraviolet ray absorbent, etc. may be added as other ingredients.

[0041]The method of forming such a hardenability constituent film 12 in the outermost layer of the inner layer board 11, Although the method of applying to the inner layer board surface and drying the method of piling up not the thing restricted especially but the film state of the hardenability constituent of which ** **** has been done, for example, or a sheet-shaped molded product on an inner layer board, or the varnish which obtained ** hardenability constituent by dissolving in a solvent, etc. are mentioned, It is preferred that a smooth field is easy to be acquired and multilayering carries out by the method of ** from an easy point.

[0042]Such film state or a sheet-shaped molded product of a hardenability constituent is usually fabricated by the solution cast method, the melting cast method, etc., and 0.5-100 micrometers of the thickness is 0.1-150 micrometers usually 1.0-80 micrometers more preferably.

[0043]It is preferred to use from a viewpoint of operativity in this invention as a dry film with a base material in which the base material is pasted together to one side of the molded product of film state, Each ingredient from which the dry film with a base material constitutes a hardenability constituent, for example, The varnish produced by mixing an organic solvent like ketones, such as hydrocarbon system solvents, such as xylene, and cyclopentanone, After applying to the 1 micrometer - 150 micrometers-thick base material which consists of metallic foils, such as thermoplastic resin films, such as a polyethylene terephthalate film, and copper foil, in accordance with a conventional method, it is obtained by carrying out dry removal of the organic solvent under 20-300 ** and heating conditions of 30 seconds - about 1 hour.

[0044]Although the method in particular of piling up such a molded product on the inner layer board 11 is not restricted, it is usually piled up under heating and a pressurizing condition. The method of heating and application of pressure has the common heat crimping (lamination) which used pressurizing machines, such as an application-of-pressure laminator device, a vacuum laminator device, a vacuum press apparatus, and a roll laminator device.

[0045]As for heating and application of pressure, it is preferred to carry out in a decompression

environment from a viewpoint [raise a wiring embeddability and] of suppressing generating of air bubbles etc. Heating and application of pressure using a pressurizing machine are performed via a press board, and usually the temperature of the press board at the time of heating and application of pressure, usually, 30-250 ** -- desirable -- 70-200 ** and crimping force -- usually -- 10kPa- 100kPa - 10MPa, and sticking-by-pressure time are usually 1 minute - 3 hours preferably 20 MPa for 30 seconds - 5 hours.

[0046]the case where heating and application of pressure are performed in a decompression environment -- usually -- 100kPa- 1 Pa of atmosphere is preferably decompressed to 40kPa-10Pa.

[0047]When the molded product which has base materials, such as a dry film with a base material, is used after forming refer to drawing 2 (b) (process B), thus the hardenability constituent film 12, After removing said base material, the compound which has the structure which can be configurated to metal in a membrane surface is contacted, and the coordination ability content compound impregnation layer 14 is formed in the surface of the hardenability constituent film 12.

[0048]In this invention, a compound which has the structure which can be configurated to metal, i.e., a coordination ability content compound, is a compound which has an unshared electron pair, and its heterocyclic compound which contains a nitrogen atom from a viewpoint of adhesion with an electrical insulation layer is preferred.

[0049]As a heterocyclic compound containing such a nitrogen atom, 1-. (2-aminoethyl) Pyrazoles, such as an imidazole-derivatives;1,3-dimethyl- 4-carboxymethyl pyrazole which is-2-methylimidazole etc.; Triazole [, such as 1-amino-2-mercapto-1,2,4-triazole,];. Triazine;, such as 2-di-n-butylamino 4,6-dimercapto S-triazine, is mentioned. These compounds may have an amino group, a thiol group, and a carboxyl group.

[0050]A method in particular of contacting such a coordination ability content compound and a hardenability constituent membrane surface is not restricted. After melting a coordination ability content compound in water or an organic solvent and making it a solution as an example, A dip method which immerses the inner layer board 11 by which the hardenability constituent film 12 was formed into this coordination ability content compound solution 13, A spray method etc. which apply this coordination ability content compound solution 13 to the surface of the hardenability constituent film 12 of the inner layer board 11 on which a Plastic solid was piled up by a spray etc. are mentioned, and even once, contact operation may repeat 2 times or more, and may perform them.

[0051]Although the temperature for contact can be arbitrarily chosen in consideration of the boiling point of a coordination ability content compound or its solution, the melting point, operativity, productivity, etc., it is usually preferably performed at 15-65 ** 10-100 **. Although contact time can be arbitrarily chosen according to the amount [the amount] of coordination

ability content compounds to make it adhere to a molded body surface, the concentration of the solution, productivity, etc., it is usually 0.1 to 60 minutes preferably for 0.1 to 360 minutes.
[0052]Then, the method of blowing inactive gas, such as nitrogen, the method of drying in oven, and after rinsing, it can be made to overheat and dry in order to remove a superfluous coordination ability content compound.
[0053]The solvent used for dissolving a coordination ability content compound, What is necessary is just to choose what a hardenability constituent film is not easily dissolved but a coordination ability content compound dissolves, For example, water; polar solvents, such as cellosolves, such as ketone, such as alcohols, such as ether, such as a tetrahydrofuran, ethanol, and isopropanol, and acetone, and ethylcellosolve acetate, are mentioned.
[0054]Although the coordination ability content compound concentration in particular in the coordination ability content compound solution 13 in this case is not restricted, a coordination ability content compound is usually 0.01 to 50 weight % preferably 0.001 to 70weight % from the viewpoint of the operativity in this process.
[0055]Drawing 2 (c) reference (the process C) a method of ranking second, hardening the hardenability constituent film 12 formed as mentioned above, and forming the electrical insulation layer 15, What is necessary is just to choose suitably according to a kind of hardening agent, and preferably, it is 100-200 ** more preferably, and 30-400 ** of cure time [70-300 ** of] is usually performed by heating preferably for 0.5 to 3 hours for 0.1 to 5 hours. A method in particular of heating in this case is not restricted, for example, what is necessary is just to perform it using oven etc. In this process C, it is thought that the layer 16 containing a compound which can be configurated to metal is formed in an inside, and the weak boundary layer 17 which consists of a low molecule ingredient is formed in the surface.
[0056]When forming a multilayered circuit board, in order to connect a conductor circuit layer in the inner layer board 11, and a conductor circuit layer formed in the process G mentioned later, before forming a metallic thin film layer, an opening for via-hole formation is formed in the electrical insulation layer 15. A method in particular of forming an opening for this via-hole formation is not restricted, for example, what is necessary is for physical processing of a drill, laser, plasma etching, etc., etc. just to perform it.
[0057]The drawing 2 (d) reference (process D) ranks second, and the process at which the mixed solution 18 which consists of potassium permanganate of prescribed concentration and hydroxylation alkali of prescribed concentration, i.e., hydrophilic processing fluid, and the surface of the electrical insulation layer 15 are contacted is performed. It is thought that the weak boundary layer 17 formed in the surface of the electrical insulation layer 15 at this process D is removed.
[0058]The mixed solution of potassium permanganate in this process D and hydroxylation alkali dissolves potassium permanganate and hydroxylation alkali in water, and is obtained by

adjusting to the following concentration.

[0059]For example, not less than 65g/l. 150g/l. or less of concentration of potassium permanganate is usually not less than 70g/l. 100g/l. or less preferably. Preferably, it is 0.95 N or more 1.2 N or less, and from before, if it is desirable that it is high concentration and they are these density ranges, as for the concentration of hydroxylation alkali, 0.75 N or more 1.5 N or less of good adhesion will usually be acquired. Hydroxylation alkali is hydroxide of an alkaline metal and sodium hydroxide and a potassium hydrate are used suitably.

[0060]The method which the method in particular of contacting the hydrophilic processing fluid 18 which consists of a mixed solution of potassium permanganate and hydroxylation alkali, and the electrical insulation layer 15 was not restricted, for example, was illustrated at the process B, and the same method are mentioned. Of course, the method of the process B and the process D may be the same, or may differ.

[0061]The time to which the solution containing potassium permanganate and hydroxylation alkali and the electrical insulation layer 15 are contacted, Usually, it is 1 minute - 7 minutes preferably, and it is more desirable than before that it is a short time for 0.5 minute - 10 minutes, and 70 ** - 90 ** of temperature is 75 ** - 85 ** preferably at the temperature of solution.

[0062]It is preferred to contact the mixed acidic solution of hydroxylamine sulfate and sulfuric acid, etc. to a substrate after this processing, and to carry out neutralization reduction processing, and also it is preferred to perform rinsing etc. after that.

[0063]Thus, after contacting the mixed solution and electrical insulation layer of potassium permanganate and hydroxylation alkali, an electrical insulation layer may be dried by the method same with having illustrated at the process B, for example.

[0064]Usually, processings, such as grant of a plating catalyst and activation of a catalyst, are performed before nonelectrolytic plating. Plating catalysts are the metallic compounds used as a reduction catalyst with the operation which a deposit of plating is made in electroless plating liquid. As metal, Pd, Pt, Au, Ag, Ir, Os, Ru, Sn, Zn, Co, etc. are mentioned.

[0065]In order to improve adhesion, Pd amine complex, sulfuric acid palladium, a palladium chloride, etc. are preferably [using a metaled generable organometallic complex and metal salt by reduction] as metallic compounds, and specifically mentioned.

[0066]After immersing metallic compounds in the liquid which dissolved in organic solvents, such as water, alcohol, or chloroform, by 0.001 to 10weight % of concentration as the method of activation of catalyst grant and a catalyst and giving a plating catalyst, the method of returning metal and activating a catalyst, etc. are mentioned. Acid, alkali, a complexing agent, a reducing agent, etc. may be contained if needed in this liquid.

[0067]The drawing 3 (e) reference (process E) ranks second, and Pd-amine complex compound catalyst 19 which is a Pd catalyst of alkali complex structure is made to stick to the

electrical insulation layer 15 produced by doing in this way.
[0068]Drawing 3 (f) 3 **, subsequently, reduction processing of the Pd-amine complex compound catalyst 19 is carried out, and the reduction plating catalyst 20 is formed.
[0069]The drawing 3 (g) reference (process F) ranks second, and the non-electrolytic copper plating layer 22 which turns into a plating seed layer using the nonelectrolytic plating method using the EDTA content plating liquid 21 containing an ethylenediaminetetraacetic acid-copper complex (EDTA-Cu) is formed.
[0070]EDTA-Cu used in order to form this non-electrolytic copper plating layer 22, EDTA of the 1.0 to 2.5 time mol concentration of Cu of 0.03 - 0.05 mol/L, and the Cu concerned, It is the solution which consisted of a solution which makes formalin of 0.01 - 0.03 mol/L basic composition, and was preferably adjusted with 0.4-0.5 N of hydroxylation alkali 0.3-0.6 N in pH adjustment. In addition, it is desirable as an additive agent to include coat improving agents, such as stabilizer, such as an alpha and alpha'-bipyridyl, or a polyethylene glycol, and a glycine.
[0071]The temperature of electroless plating liquid of the conditions which form a metallic thin film layer is for 50-70 **, and 20 micrometers of plating thickness are preferably chosen suitably from 0.1 micrometer by the range of 0.3 to 10 micrometers.
[0072]On the drawing 3 (h) reference (process G) non-electrolytic copper plating layer 22 which ranked second and was formed in the process E, For example, make plating resist (a graphic display is omitted) form in accordance with a conventional method, and also on it, make it grow up electrolytic copper plating layer 23 with wet plating, such as electrolysis plating, and it ranks second, Plating resist is removed, etching removes the non-electrolytic copper plating layer 22 to expose further, and a conductor circuit layer (a graphic display is omitted) is formed. This conductor circuit layer will comprise the electrolytic copper plating layer 23 which formed membranes the non-electrolytic copper plating layer 22 and on it.
[0073](Process H) Since it ranks second and the adhesion of a conductor circuit layer is improved in this invention, the inner layer board 11 in which the non-electrolytic copper plating layer 22 was formed, and the inner layer board 11 by which the conductor circuit layer was formed on the non-electrolytic copper plating layer 22 can be heated, for example using oven, a hot air drying furnace, etc. The neighborhood of glass-transition temperature of temperature conditions of the electrical insulation layer 15 is desirable, and they are usually 80-250 ** preferably 50-350 **.
[0074]In this way, a multilayered circuit board obtained can be used in electronic devices, such as a computer and a cellular phone, as a printed wired board for mounting a mounting component of semiconductor devices, such as CPU and a memory, and others. Especially a thing that has fine wiring is preferred as a high-density printed-circuit board as a wiring board of a high speed computing machine and a personal digital assistant used in a high frequency

region.

[0075]Although an working example and a comparative example are given to below and specific constitution of this invention is explained to it, a valuation method performed in this example before that is explained. Among each working example, a part and % are weight references, as long as there is no notice especially. The valuation method performed in this example is as follows.

** A molecular weight (Mw, Mn) : it measured as a polystyrene reduced property by a gel permeation chromatography (GPC) which uses toluene as a solvent.

A hydrogenation rate and (anhydrous) maleic-acid-residue content : ** The inside of a polymer before hydrogenation, the number of mols of maleic acid residue to the total number of monomeric units (anhydrous) in a hydrogenation rate (hydrogenation appending rate) over the number of mols of an unsaturated bond, and a polymer -- it measured with a ^{1}H-NMR spectrum comparatively (carboxyl group content).

** Glass transfer temperature (Tg) : it measured with a differential scanning calorimetry method (the DSC method).

** Evaluation of plating adhesion : after performing electrolysis plating and forming an 18-micrometer-thick electrolytic copper plating film, according to the peel strength of the copper foil provided in JIS (JIS C 6481), the peel strength examination estimated evaluation of the adhesion of 170 ** the heat-treated conductor circuit for 30 minutes 90 degrees.

** Evaluation of surface roughness : the tapping mode in the atmosphere measured and estimated surface average-of-roughness-height Ra using the Si-single-crystal stick-shape cantilever (load rate = 20 N/m and 125 micrometers in length) with the atomic force microscope (trade name made from Nanoscope 3 a:Digital Instrument).

[0076]Below, a concrete working example and a comparative example are explained on the assumption that the above matter.

(Working example 1) As a hardenability constituent, the ring-opening-polymerization object of 4.4.0.1^{2} and 8-ethyl-tetracyclo [5.1^{7,10}] dodec-3-ene is hydrogenated first, The denaturation hydrogenation polymer produced by furthermore carrying out maleic anhydride denaturation (Mn=33,200, Mw=68,300, Tg = 170 **) Maleic-acid-residue content =25 mol %100 copy, 40 copies of bisphenol A bis(propylene glycol glycidyl ether)ether, Five copies of 2-[2-hydroxy-3,5-bis(alpha and alpha-dimethylbenzyl)phenyl] benzotriazols and 0.1 copy of 1-benzyl-2-phenylimidazole were dissolved in the partially aromatic solvent which consists of 215 copies of xylene, and 54 copies of cyclopentanones, and the varnish was obtained.

[0077]Subsequently, coat the varnish concerned using a die coater on the carrier film which consists of a polyethylenenaphthalate film with a thickness of 40 micrometers of 300 mm squares, and in nitrogen oven after that, For example, it dried for 10 minutes at 120 **, and the dry film with a carrier film with a resin thickness of 40 micrometers was obtained.

[0078]On the other hand, the 0.1% isopropyl alcohol solution of 2-di-n-butylamino 4,6-dimercapto S-triazine is prepared, Wiring width and inter wiring distances in this solution 50 micrometers, Conductor thickness immerses a double-sided copper-clad board (core material produced by making glass fabrics impregnate the varnish containing a glass filler and a halogen-free epoxy resin) with a thickness of 0.8 mm which had the inner layer circuit where the micro etching process of the surface was carried out formed at 18 micrometers for 1 minute at 25 **, Subsequently, made it dry in the oven by which the nitrogen purge was carried out for 15 minutes at 90 **, the primer layer was made to form, and the inner layer board was obtained.

[0079]Subsequently, on this inner layer board, the above-mentioned dry film with a carrier film was piled up to double-sided copper-clad board both sides, as the resin surface became the inside. This is decompressed to 200 Pa using the vacuum laminator provided with the press board made of heat-resistant rubber up and down, After carrying out heat crimping for 60 seconds by the temperature of 125 **, and pressure 0.5MPa and forming a hardenability constituent film on an inner layer board, only the polyethylenenaphthalate film was removed from the substrate with which this hardenability constituent film was formed.

[0080]Subsequently, after making the solution adjusted so that 1-(2-aminoethyl)-2-methylimidazole (AMZ) might be 0.3% immerse for 10 minutes at 25 **, repeat being immersed for 1 minute in another tank 3 times, rinse it in it, and it ranks second to it, After the air knife removed the excessive solution, this was neglected for 60 minutes in 170 ** nitrogen oven, and the electrical insulation layer was formed on the inner layer board. The result of having evaluated the electrical insulation layer surface roughness in this state is shown in drawing 4.

[0081]Subsequently, using the ultraviolet rays which become an electrical insulation layer of the substrate in which the electrical insulation layer was formed from the 3rd harmonics (THG) of an YAG laser, the via hole for an interlayer connection 30 micrometers in diameter was formed, and the layered substrate with a via hole was obtained.

[0082]Subsequently, this layered substrate with a via hole was immersed in the 80 ** solution adjusted so that it might become the permanganic acid concentration of 80g/l., and the sodium hydroxide concentration of 40g/l. for 5 minutes.

[0083]Subsequently, by repeating twice that a substrate is immersed in a tank for 1 minute, and also irradiating with an ultrasonic wave for 2 minutes in 25 ** another tank, After rinsing a substrate, immersing a substrate in the 45 ** solution adjusted so that it might become hydroxylamine sulfate concentration of 20g/l., and 50g/l. of sulfuric acid for 5 minutes and carrying out neutralization reduction processing to it, hot water rinsing was carried out at 60 ** for 10 minutes.

[0084]PURIDIPPUNEOGANTO B (trade name made from ATOTEKKU, Inc.) a layered substrate after hot water rinsing Subsequently, 20ml/l. In a PURIDIPPU solution adjusted so

that it might become the sulfuric acid concentration of 1ml/l., 25 **, After being immersed for 1 minute, it was immersed in 50 ** Pd salt content plating catalyst solution adjusted so that it might be set to pH=11.0 with activator neo GANTO 834 concentrated (trade name made from ATOTEKKU, Inc.) 30ml/l., boric acid concentration of 5g/l., and sodium hydroxide concentration for 5 minutes.

[0085]Subsequently, after rinsing a substrate by same method as ****, it was immersed in a solution adjusted so that it might become reducer neo GANTO WA(trade name made from ATOTEKKU, Inc.)5ml/l., and 25 g/liter boric acid concentration for 5 minutes at 30 **, and reduction processing of the plating catalyst was carried out.

[0086]An obtained layered substrate as the metal Cu In this way, 2.3g/l. 20g [l.] /, the formalin 1.0g/l. is made into basic composition for EDTA, Blowing air into electroless plating liquid which consists of non-electrolytic copper plating liquid KC-500 (trade name by Japan Energy, Inc.) which adjusted pH to 12.5 in sodium hydroxide, it was immersed for 15 minutes, nonelectrolytic plating processing was carried out, and temperature of 60 ** formed a metallic thin film layer.

[0087]Subsequently, the layered substrate in which the metallic thin film layer was formed by this nonelectrolytic plating processing was rinsed still like ****. Subsequently, after being immersed for 1 minute in the inhibited de-rusting solution adjusted so that OPC Defencer (trade name by Okuno Pharmaceuticals incorporated company) might become [l.] in 8ml /and also rinsing 25 ** by the same method as **** to it, it dried and rust prevention treatment was performed.

[0088]Subsequently, the dry film of the commercial photosensitive resist was bonded by thermo-compression and stuck on the layered substrate surface on which this rust prevention treatment was performed, negatives were developed and the resist pattern was obtained, after sticking the mask of the pattern corresponding to the pattern for adhesion evaluation on this dry film and exposing further.

[0089]Subsequently, after making the solution of 100g/l. of sulfuric acid immerse for 1 minute at 25 ** and removing rust preventives, electrolytic copper plating was selectively performed for the resist pattern as a mask, and, for example, thickness made an 18-micrometer electrolytic copper plating film form.

[0090]Subsequently, by performing an etching process with a cupric chloride and a chloride mixed solution, after carrying out the strip of the resist pattern with release liquid, The circuit pattern (conductor circuit layer) which removes the exposed part of a metallic thin film layer, and consists of an electrolytic copper plating film / a metallic thin film layer was formed, and it ranked second, and also heat-treated in oven for 170 ** 30 minutes, and the double-sided two-layer multilayered circuit board with a circuit pattern was obtained. The evaluation result of the plating adhesion of the obtained multilayered circuit board is shown in drawing 4.

[0091]Thus, in an working example 1 of this invention, with 34 nm, although granularity R_a of the surface of the electrical insulation layer 15 is dramatically flat, Since nonelectrolytic plating processing of a hydrophilization treatment-EDTA type of formation-high concentration and a short time of a layer containing a compound which can be configurated to metal was performed as a series of processes, adhesion strength 593 gf/cm of a grade which is satisfactory practically was able to be obtained.

[0092]Next, although an working example 2 is described, thing explanation with other composition completely equivalent to the above-mentioned working example 1 only by changing concentration in AMZ processing in an working example 1 is simplified.

(Working example 2) Only a polyethylenenaphthalate film is removed after forming a hardenability constituent film like an working example 1, Instead of making solution adjusted so that 1-(2-aminoethyl)-2-methylimidazole in an working example 1 might be 0.3% immerse for 10 minutes at 25 **, Except making solution adjusted so that it might become 1.0% immerse for 10 minutes at 25 **, it carried out like an working example 1 and a double-sided two-layer multilayered circuit board with a circuit pattern was obtained.

[0093]An evaluation result of the plating adhesion of an obtained multilayered circuit board is shown in drawing 4. Thus, in an working example 2 of this invention, although concentration of AMZ was raised about 3.3 times, adhesion strength of the almost same 574 gf/cm as the above-mentioned working example 1 was obtained. However, since concentration of AMZ was high, surface roughness R_a of an electrical insulation layer increased.

[0094](Comparative example 1) After forming a hardenability constituent film on an inner layer board in a method shown in an working example 1, and a similar way, only a polyethylenenaphthalate film was removed from a substrate with which the above-mentioned hardenability constituent was formed. Subsequently, this was neglected for 60 minutes in 170 ** nitrogen oven, and an electrical insulation layer was formed on an inner layer board. A result of having evaluated electrical insulation layer surface roughness at this time is shown in drawing 4.

[0095]Subsequently, the plating adhesion of a multilayered circuit board obtained by the same method as an working example 1 by obtaining a double-sided two-layer multilayered circuit board with a circuit pattern was evaluated. A result of peel strength is shown in drawing 4.

[0096]Thus, in the comparative example 1, since AMZ processing is not performed but only hydrophilization treatment is performed, only adhesion strength of about 243 gf/cm is obtained, but it is understood from this point that AMZ processing is indispensable.

[0097](Reference example 1) A plating catalyst is given to the layered substrate with a via hole which formed the electrical insulation layer on the inner layer board in the method shown in the working example 1, and the similar way, Blowing air into the non-electrolytic copper plating liquid which consists of metallic copper concentration =2.5g/l., Rochell salt =28g/l., formalin

=20g/l., and NaOH=1.5g/l. the layered substrate which carried out reduction processing. It was immersed for 15 minutes and 36 ** of plating solution temperature formed the metallic thin film layer on the layered substrate.

[0098]The following processes evaluated the plating adhesion of the multilayered circuit board obtained with the same disposal method as the working example 1 by obtaining a double-sided two-layer multilayered circuit board with a circuit pattern. The result of peel strength is shown in drawing 4.

[0099]Thus, in the reference example 1, as a result of forming a plating seed layer using another electroless plating liquid, it turned out that peel strength is about 189 gf/cm. From this point, it is understood that it is effective as electroless plating liquid in a nonelectrolytic plating process to use EDTA content plating liquid.

[0100]As mentioned above, although the embodiment of the invention has been described, this invention is not restricted to the composition and the conditions indicated to the embodiment, and various kinds of change is possible for it. For example, in the above-mentioned working example, although explained as a manufacturing process of a multilayer printed circuit board, it is not restricted to a multilayer printed circuit board, and is applied also to the interposer made to intervene between a printed-circuit board and a semiconductor chip.

[0101]As an inner layer board, a semiconductor substrate is also contained and it is applied to a semiconductor integrated circuit device also at multilayer interconnection structure. That is, each element which constitutes a semiconductor integrated circuit device is increasingly miniaturized with high integration of a semiconductor device, or improvement in the speed, and the density of the current which also pours wiring in connection with it to a densification, the stress applied to wiring while multilayering and thin-film-izing, or wiring is increasing increasingly in recent years.

[0102]Since the fracture phenomenon of wiring called electromigration occurs by sending high-density current through wiring, in connection with the miniaturization of an element, the wiring material with high reliability which can send higher-density current is needed.

[0103]A manufacturing process is easy, since it is low cost, aluminum is used as a wiring material of an integrated circuit device until now, but. Since it is necessary to control increase of the signal delay accompanying a miniaturization, since aluminum of 2.70micro ohm-cm is not necessarily low resistance enough, electrical resistivity, Electrical resistivity is smaller than aluminum, and adoption of Cu (electrical resistivity: 1.55micro ohm-cm) whose electromigration resistance is twice [about] the aluminum is considered.

[0104]In order to reduce signal delay with the miniaturization and wiring-density-izing of a wiring layer, lower-dielectric-constant-izing of an interlayer insulation film is indispensable, but. it becomes lower dielectric constant-ization of an interlayer insulation film by using the electrical insulation layer of this invention -- both, It becomes possible to improve the adhesion

of a wiring layer by using Cu plating film accompanied by an AMZ processing-hydrophilization treatment-EDTA nonelectrolytic plating process, and further, when forming the whole by a low temperature process 500 ** or less, it becomes a formation method of dominance multilayer interconnection structure.

[0105]

[Effect of the Invention]Since according to this invention a series of processes of consisting of an AMZ processing-hydrophilization treatment-EDTA nonelectrolytic plating process are performed when forming a conductor circuit layer in an electrical insulation layer with plating, Without carrying out roughening treatment of the surface of an electrical insulation layer, adhesion strength which can be equal to practical use can be realized, and realization of the multilayer interconnection board for the high-speed transmission of a GHz order is attained by it.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

CLAIMS

[Claim(s)]
[Claim 1]After forming in the outermost layer of an inner layer board a hardenability constituent film which consists of an insulating polymer and a hardening agent, contact a compound which has the structure which can be configurated to metal to said hardenability constituent membrane surface, and it ranks second to it, After stiffening this hardenability constituent film and forming an electrical insulation layer, perform hydrophilization treatment on the surface of said electrical insulation layer, and it ranks second to it, A formation method of multilayered circuit structure having the process of forming a conductor circuit layer containing said metallic thin film layer after using an ethylenediaminetetraacetic acid-copper complex for the surface of said electrical insulation layer and forming a metallic thin film layer in it.
[Claim 2]The above-mentioned hydrophilization treatment process, A formation method of the multilayered circuit structure according to claim 1 being the process of contacting a mixed solution which consists of not less than 65g/l. 150g/l. or less of potassium permanganate, and 0.75-N or more hydroxylation alkali of 1.5 N or less, and said electrical insulation layer, and carrying out the surface treatment of the electrical insulation layer.
[Claim 3]A hardenability constituent film which consists of an insulating polymer formed in the outermost layer of the above-mentioned inner layer board, and a hardening agent, or [piling up either / which consists of an insulating polymer and a hardening agent / film state of a hardenability constituent, or a sheet-shaped Plastic solid on said inner layer board, and forming it] -- or, A formation method of the multilayered circuit structure according to claim 1 or 2 forming by one method of whether it dries and forms after applying to said inner layer board surface a varnish which obtained a hardenability constituent which consists of said insulating polymer and a hardening agent by dissolving in a solvent.
[Claim 4]A formation method of a multilayered circuit structure given in any 1 clause of Claims 1-3 having the process of heating an inner layer board in which said conductor circuit layer

was formed after a process of forming the above-mentioned conductor circuit layer.
[Claim 5]A base substance which has the multilayered circuit structure having the multilayered circuit structure manufactured by a formation method of a multilayered circuit structure given in any 1 clause of Claims 1-4.

[Translation done.]

* NOTICES *

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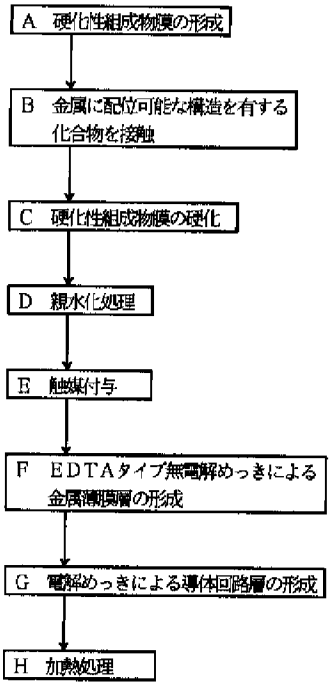
DRAWINGS

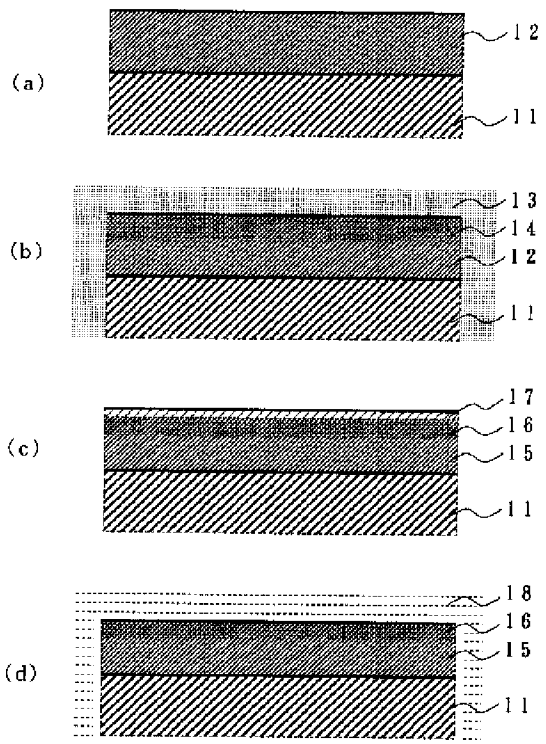
[Drawing 1]

本発明の原理的構成を示すフロー図



[Drawing 2]

本発明の実施の形態の途中までの製造工程の説明図



11: 内層基板
12: 硬化性組成物膜
13: 配位能含有化合物溶液
14: 配位能化合物含浸層
15: 電気絶縁層
16: 金属に配位可能な化合物を含有する層
17: 弱境界層
18: 親水処理液

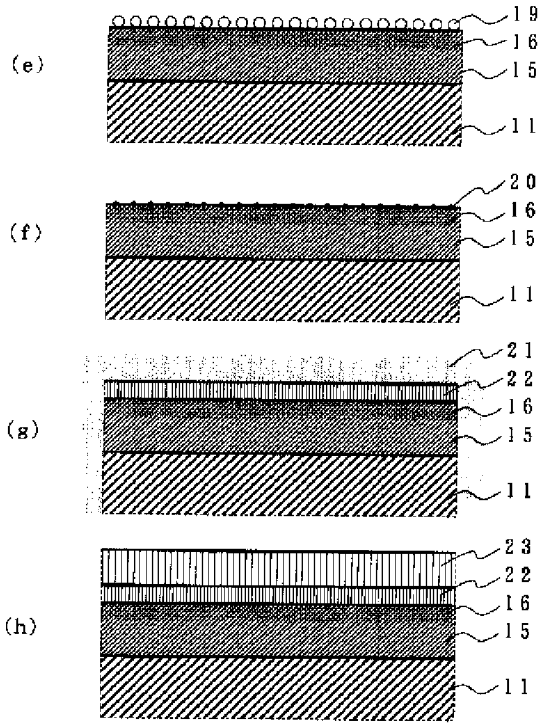
[Drawing 4]

本発明の各実施例、比較例、及び、参考例
における密着強度及び表面粗さR_aの説明図

	ピール強度 [gf/cm]	表面粗さR_a [nm]
実施例1	593	34
実施例2	574	109
比較例1	243	14
参考例1	189	34

[Drawing 3]

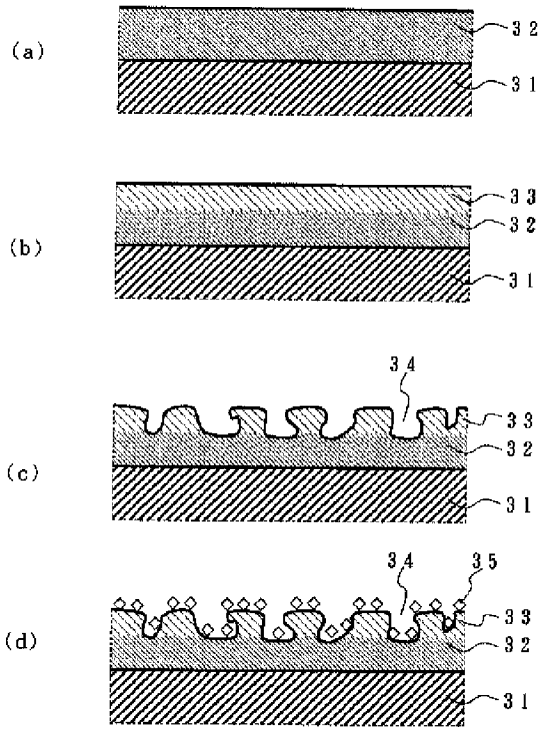
本発明の実施の形態の図２以降の製造工程の説明図



11: 内層基板
15: 電気絶縁層
16: 金属に配位可能な化合物を含有する層
19: Ｐｄ－アミン錯体触媒
20: 還元めっき触媒
21: ＥＤＴＡ含有めっき液
22: 無電解銅めっき層
23: 電解銅めっき層

[Drawing 5]

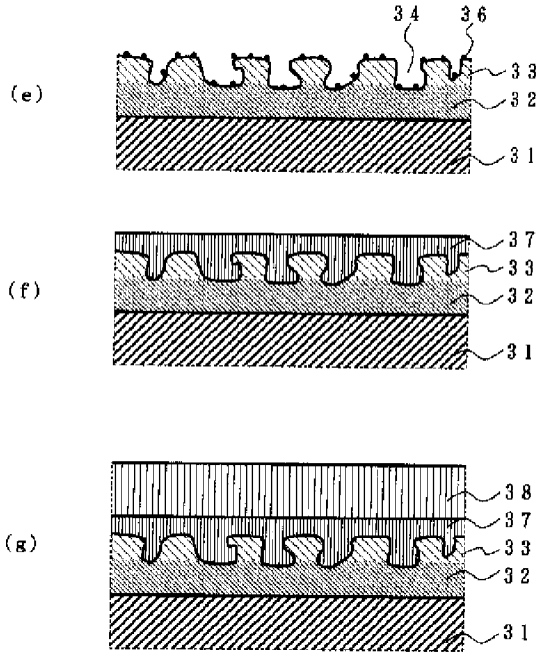
従来の多層回路基板の途中までの製造工程の説明図



31:両面銅張積層板
32:エポキシ樹脂層
33:膨潤層
34: 凹凸
35: $(Pd)_m (Sn)_n Cl^-$

[Drawing 6]

従来の多層回路基板の図5以降の製造工程の説明図

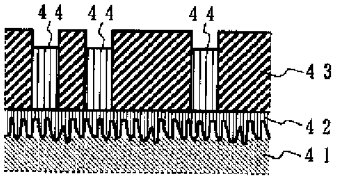


31:両面銅張積層板
32:エポキシ樹脂層
33:接着層
34:凹凸
36: Pd触媒
37: 無電解銅めっき層
38: 電解銅めっき層

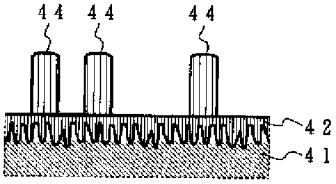
[Drawing 7]

従来の粗化処理に伴う問題点の説明図

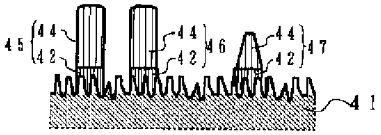
(a)



(b)



(c)



41: 樹脂層
42: 無電解銅めっき層
43: めっきレジストパターン
44: 電解銅めっき層
45: 配線
46: 配線
47: 配線

[Translation done.]

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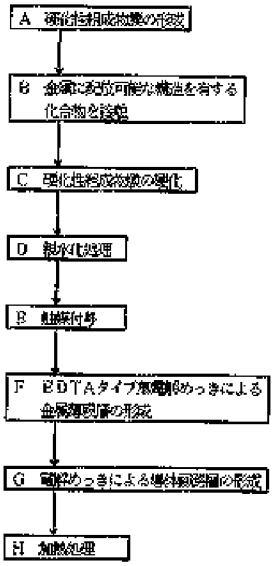
最終頁に続く

(54)【発明の名称】　多層回路構造の形成方法及び多層回路構造を有する基体

(57)【要約】
【課題】　多層回路構造の形成方法及び多層回路構造を有する基体に関し、電気絶縁層の表面を平坦にしたままで導電体回路層の密着性を向上する。
【解決手段】　内層基板の最外層に、絶縁性重合体と硬化剤とからなる硬化性組成物膜を形成した後、前記硬化性組成物膜表面に、金属に配位可能な構造を有する化合物を接触させ、次いで、当該硬化性組成物膜を硬化させて電気絶縁層を形成した後、得られた電気絶縁層の表面に親水化処理を行い、次いで、前記電気絶縁層の表面にエチレンジアミン四酢酸－銅錯体を用いて金属薄膜層を形成したのち、前記金属薄膜層を含む導電体回路層を形成する。

本発明の製造方法を示すフロー図



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【特許請求の範囲】

【請求項１】　内層基板の最外層に、絶縁性重合体と硬化剤とからなる硬化性組成物膜を形成した後、前記硬化性組成物膜表面に、金属に配位可能な構造を有する化合物を接触させ、次いで、該硬化性組成物膜を硬化させて電気絶縁層を形成したのち、前記電気絶縁層の表面に親水化処理を行い、次いで、前記電気絶縁層の表面にエチレンジアミン四酢酸－銅錯体を用いて金属薄膜層を形成したのち、前記金属薄膜層を含む導電体回路層を形成する工程を有することを特徴とする多層回路構造の形成方法。

【請求項２】　上記親水化処理工程が、６５ｇ／リットル以上１５０ｇ／リットル以下の過マンガン酸カリウム及び０．７５規定以上１．５規定以下の水酸化アルカリからなる混合溶液と前記電気絶縁層とを接触させて電気絶縁層を表面処理する工程であることを特徴とする請求項１記載の多層回路構造の形成方法。

【請求項３】　上記内層基板の最外層に形成された絶縁性重合体と硬化剤とからなる硬化性組成物膜を、絶縁性重合体と硬化剤とからなる硬化性組成物のフィルム状又はシート状成形体のいずれかを前記内層基板に重ね合わせて形成するか、或いは、前記絶縁性重合体と硬化剤とからなる硬化性組成物を溶剤に溶解して得たワニスを前記内層基板表面に塗布したのち乾燥して形成するかのいずれかの方法で形成したことを特徴とする請求項１または２に記載の多層回路構造の形成方法。

【請求項４】　上記導電体回路層を形成する工程の後に、前記導電体回路層を形成した内層基板を加熱する工程を有することを特徴とする請求項１乃至３のいずれか１項に記載の多層回路構造の形成方法。

【請求項５】　請求項１乃至４のいずれか１項に記載の多層回路構造の形成方法によって製造された多層回路構造を有することを特徴とする多層回路構造を有する基体。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】本発明は多層回路構造の形成方法及び多層回路構造を有する基体に関するもので、より詳しくは、配線パターン密着性に優れ、かつ平滑な電気絶縁層上に導電体回路層を形成するための処理工程に特徴のある多層回路構造の形成方法及び多層回路構造を有する基体に関するものである。

【０００２】

【従来の技術】電子機器の小型化、多機能化に伴って、電子機器に用いられている回路基板にも、より高密度化が要請されるようになってきている。この様な回路基板の高密度化の要請に応えるためには、回路基板を多層化するのが一般的である。

【０００３】多層回路基板は、通常、最外層に導電体回路層が形成された内層基板の表面に、電気絶縁層を積層し、当該電気絶縁層の上に新たな導電体回路層を形成することによって得られ、さらに必要に応じて電気絶縁層と導電体回路とを数段積層することもできる。

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【０００４】この様な多層回路基板においては、多層回路基板の寿命を確保するため、電気絶縁層と、その上に形成する導電体回路パターンとの密着性、即ち、パターン密着性が重要となっている。

【０００５】そこで、この様なパターン密着性を得る方法として、電気絶縁層を粗化する各種の方法（必要ならば、特開平１１－２３６４９号公報、特開平１１－２８６５６２号公報、特許第２８７７１１０号公報参照）が広く採用されているので、ここで、図５及び図６を参照して、その一例を説明する。

【０００６】図５（ａ）参照

例えば、表面に銅回路（図示を省略）を設けた両面銅張積層板３１上にエポキシ樹脂層３２をラミネートしたのち、紫外レーザ光を照射して両面銅張積層板３１に設けた銅回路に接続するためのビアホール（図示を省略）を形成する。

【０００７】図５（ｂ）参照

次いで、ＮａＯＨと界面活性剤を主成分とした溶液中に浸漬してエポキシ樹脂層３２を膨潤処理する。この膨潤処理によって、エポキシ樹脂層３２の表面に膨潤層が形成される。

【０００８】図５（ｃ）参照

次いで、$KMnO_4$とＮａＯＨの混合溶液からなる酸化性溶液であるデスミア処理溶液中に両面銅張積層板３１を浸漬することによって、ビアホール内部のレーザ加工において発生した残渣を除去するとともに、エポキシ樹脂層３２の表面に微細な凹凸を形成する。

【０００９】次いで、両面銅張積層板３１を水洗処理したのち、ヒドラジンを含む中和溶液中に両面銅張積層板３１を浸漬して中和処理し、次いで、再び、両面銅張積層板３１を水洗処理したのち、脱脂溶液中に両面銅張積層板３１を浸漬して脱脂処理を行う。

【００１０】図５（ｄ）参照

次いで、両面銅張積層板３１を水洗処理したのち、プリディップ液中に浸漬して、次工程のキャタリスト工程におけるキャタリスト液とのなじみを改善し、次いで、両面銅張積層板３１を水洗処理したのち、キャタリスト液中に浸漬して、銅回路、エポキシ樹脂層３２、及び、膨潤層３３の露出表面に、ＳｎとＰｄのコロイド物質［$(Pd)_m(Sn)_n(Cl)_p^-$］３５を析出させる。

【００１１】図６（ｅ）参照

次いで、両面銅張積層３１板を水洗処理したのち、アクセレーター液中に浸漬してコロイド物質中のＳｎを離脱させて、銅回路、エポキシ樹脂層３２、及び、膨潤層３３の露出表面に、Ｐｄ触媒３６のみを付着させる。

【００１２】図６（ｆ）参照

次いで、両面銅張積層板３１を水洗処理したのち．硫酸銅を主成分とする硫酸銅系の無電解銅めっき液を用いて無電解銅めっき処理を施すことによって、銅回路．エポキシ樹脂層３２．及び、膨潤層３３の露出表面に無電解銅めっき層３７からなるめっきシード層を形成する。

【００１３】図６（ｇ）参照

次いで、無電解銅めっき層３７を形成した両面銅張積層板３１に電解銅めっき処理を施すことによって露出するめっきシード層上に電解銅めっき層３８を形成するとともにビアホールを埋め込み．次いで、電解銅めっき層３８及び無電解銅めっき層３７を所定パターンにエッチングすることによって銅配線を形成する。この工程を必要とする回数繰り返すことによって、多層回路基板が完成する。

【００１４】また、密着性を改良する他の手段としては．粗化後の電気絶縁層上に、ゴムや樹脂などの高分子成分を含有する無電解めっき用接着剤を塗布することも検討されている（必要ならば、特開２００１－１９２４４号公報、特開２００１－１２３１３７号公報．特開平１１－４０６９号公報等参照）。

【００１５】さらに、本出願人等は．樹脂層としてポリイミドを用いると共に、ポリイミドの開環残基に金属イオンを吸着・還元することによって．実用上必要とされている密着強度０．６ｋｇｆ／ｃｍを達成している（必要ならば、熊本県地域結集型共同研究「超精密半導体計測技術開発」第２回技術シンポジウム、２００１参照）。

【００１６】しかしながら．こうした電気絶縁層が形成された後の処理によっては．温度や湿度の変化のある場合に十分なパターン密着性が必ずしも得られず．回路基板の寿命を短くすることや．粗化面の表面粗さが小さくなると密着性が低く、信頼性が低下したりすることがあった。

【００１７】また、上述のような粗化した電気絶縁層上に形成した導電体層をエッチング液により導電体回路を形成する場合．導電体回路の間隔の広狭によりエッチング液の入り込みやすさが異なるため導電体回路の加工精度が悪くなるという問題があるので．この事情を図７を参照して説明する。

【００１８】図７（ａ）参照

粗化処理した樹脂層４１上に無電解めっき法により無電解銅めっき層４２を形成したのち、めっきレジストパターン４３を利用して電解めっき法によって電解銅めっき層４４を形成する。

【００１９】図７（ｂ）参照

次いで、めっきレジストパターン４３を除去したのち、露出する無電解銅めっき層４２を除去して、電解銅めっき層４４／無電解銅めっき層４２からなる配線４５～４７を形成するとともに、各配線４５～４７を電気的に分離する。

【００２０】図７（ｃ）参照

しかし、配線４５，４６の相互間隔が狭い所ではエッチング液の流れがスムーズではなく、エッチングレートが低下するため．露出する無電解銅めっき層４２を完全に除去して各配線４５，４６を電気的に分離するためにはエッチング時間を長くする必要がある。特に、樹脂層４１の表面を粗化しているので、無電解銅めっき層４２の厚さは凹部を埋め込んだ部分では３～８μｍになり、この３～８μｍの無電解銅めっき層４２を除去するためにエッチング時間が長くなる。

【００２１】そうすると．配線４６．４７の相互間隔が広い所ではエッチング液の流れがスムーズになるのでエッチングレートが高くなり．配線４７が過剰エッチングされて、パターン形状が劣化して加工精度が低下することになる。

【００２２】さらには、密着性改善するために電気絶縁層の表面を粗化した場合．形成された導電体回路層が非平坦になるので．導電体回路の電気信号伝送特性はＧＨｚ以上の高周波領域においては表皮効果の影響により悪化するという問題がある。因に、１ＧＨｚの場合には、導体層の表面から２μｍ程度の厚さに集中するため、表面の凹凸が大きいと実効的伝送路長が長くなり．電気信号伝送特性が悪化することになる。

【００２３】

【発明が解決しようとする課題】この様な問題を改善するために、本発明者の一人は、樹脂層の表面を粗化することなく配線を形成する際に、密着性の低下の問題を改善するために樹脂層の表面に金属に配位可能な化合物を含有する層を形成することで、密着性を確保できることを見いだしている（必要ならば、特願２００１－２６８８４７号参照）。

【００２４】そこで、今回．本発明者等は、この方法におけるめっき条件に着目し．密着性の指標の一つであるピール強度を向上させるための検討を行った。

【００２５】

【課題を解決するための手段】図１は．本発明の原理的構成を示すフロー図であり．ここで．図１を参照して本発明における課題を解決するための手段を説明する。図１参照（１）本発明は、多層回路構造の形成方法において．内層基板の最外層に．絶縁性重合体と硬化剤とからなる硬化性組成物膜を形成した（工程Ａ）後、前記硬化性組成物膜表面に、金属に配位可能な構造を有する化合物を接触させ（工程Ｂ）．次いで、当該硬化性組成物膜を硬化させて電気絶縁層を形成した（工程Ｃ）後．得られた電気絶縁層の表面に親水化処理を行い（工程Ｄ）、次いで、前記電気絶縁層の表面にエチレンジアミン四酢酸－銅錯体を用いて金属薄膜層を形成した（工程Ｆ）のち．前記金属薄膜層を含む導電体回路層を形成する（工程Ｇ）各工程有することを特徴とする。

【００２６】この様に、本発明者らは．平滑な電気絶縁